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Magneto-Optical Characterization of Excited States in C_{60}

by

**X. Wei, Z.V. Vardeny, D. Moses, V.I. Srdanov,
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Magneto-Optical Characterization of Excited States in C_{60}

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Abstract

We have used various optical and optically detected magnetic resonance techniques to characterize excited states in C_{60} in toluene/polystyrene (T/PS) glass and C_{60} films produced by evaporation. In C_{60}: T/PS glass at 4K we found long lived (~ 5 ms) triplet excitons which recombine radiatively with a linear kinetics. Their relatively small zero-field-splitting (ZFS) parameters indicate delocalization over the entire C_{60} molecule. In C_{60} film, however, we found both neutral and charged excitations, with bimolecular recombination kinetics. The neutral photoexcitations are more delocalized triplets with smaller ZFS, whereas the charge carriers are spin ½ excitations which we identified as C_{60}^x due to their optical transitions and associated photoinduced electroabsorption.

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Since the fullerenes and in particular C_{60} became available in quantity [1], they have stimulated a great deal of experimental work. Most dramatically, C_{60} films show superconductivity at T_c as high as 47K [2,3] when doped with alkali metals. The structure of C_{60} and its aromaticity have been convincingly demonstrated with good agreement between experiment and theory [4]. Photoexcitation (or photo-doping) provides a means of charge injection at a very low concentration and this may help in separating intramolecular and intermolecular interactions in C_{60} films. Although several studies of excited states in C_{60} solutions have been recently reported [5-8], the nature of the photoexcitations in C_{60} solids, where the intermolecular interaction is more important, have yet to be identified [9-12].

In this work we characterize the photoexcitations in C_{60} in toulene/polystyrene (T/PS) glass and thin films produced by evaporation, using various optical and magneto-optical techniques. They include photomodulation (PM), photoluminescence (PL), and their optically detected magnetic resonance: the absorption detected magnetic resonance (ADMR) and the PL detected magnetic resonance (PDMR), respectively. We measured in C_{60}: T/PS glass long lived ($\sim$5ms) triplet excitons with photoinduced absorption (PA) bands in the triplet manifold at 1.65 and 1.8 eV, respectively, which recombine with linear kinetics. These triplets give rise to a triplet PL component and have relatively small zero-field-splitting (ZFS) parameters of $D = 0.0115$ cm^{-1} and $E = 0.0008$ cm^{-1}, respectively, indicating delocalization over the entire C_{60} molecule. In C_{60} films, however, we measured both neutral and charged excitations, with bimolecular recombination kinetics. The neutral excitations form more delocalized triplet excitons with somewhat different PA bands and smaller ZFS parameters ($D = 0.0098$ cm^{-1})

whereas the charged carriers are spin ½ excitations, with PA bands at 0.8 and 2 eV, respectively and a correlated electroabsorption due to the photogenerated electric fields in the film. Based on C_{60} energy levels calculation [13] we identify the charged photoexcitations as $C_{60}^{\mp}$.

The PM and PL spectra have been excited by an Ar^+ laser beam at 458 nm (pump) with intensity $I_L \approx 400$ mWcm^{-2} modulated at frequency f ranging from 20 Hz to 50 kHz by an acousto-optical modulator. The PL from the sample and the transmission of a cw lamp (probe beam) were dispersed by a ¼ met. monochromator and measured by various solid state detectors in the spectral range of 0.3 to 2.7 eV. For the ADMR measurements the pump and probe beams constantly illuminate the sample mounted in a high Q microwave cavity at 3 GHz equipped with optical windows and a superconducting magnet producing a field H up to 3 Tesla. Microwave (μ-wave) resonant absorption modulated at a frequency between 20 to 4 KHz leads to small changes δT in the transmission T proportional to the change in photoexcitation density n produced by the pump beam. δn is induced by transitions in the μwave range that charge spin-dependent recombination rates. With suitable signal averaging, the system δT/T sensitivity was about 10^{-7}. In PDMR we measure changes δL in the PL intensity L with sensitivity δL/L ~ 10^{-6}.

5. Two types of ADMR (PDRM) spectra were obtained: the H-ADMR spectrum, in which δT (δL) is measured at a fixed probe wavelength λ while sweeping H, and the P-ADMR spectrum in which δT is measured at a constant H, in resonance, while λ (probe) is varied.

Purified C_{60} powder, with purity better than 99%, as established by Raman scattering spectroscopy [14], was mixed in a solution of degassed toluene/polystyrene which was

subsequently evaporated to form C_{60}: T/PS glass. The C_{60} films, however, were deposited at

450 C on sapphire substrates by evaporation at 5×10^{-6} torr [15]. The film thickness (1000Å to

2 μm) was controlled by the deposition time. X-ray diffraction and low resolution atomic force

micrographs showed essentially amorphous to nanocrystalline type samples.

The optical and magneto-optical measurements of C_{60}: T/PS glass at 4K are shown in Fig.

1. The PM spectrum contains a strong PA band (T_1) which peaks at 1.65 eV [7,8] and a

shoulder (T_2) at 1.8 eV. Both PA bands increase linearly with I_L showing monomolecular

recombination kinetics. The H-ADMR spectrum at 1.65 eV (Fig. 1, lower inset) shows a 200

G wide triplet powder pattern at "full field" ($\Delta m_s = \pm 1$) around H = 1071 G with $\delta n/n = -6$

$\times 10^{-3}$, and a narrow (5 G) signal at "half field" ($\Delta m_s = \pm 2$) peaked at 531 G. To correlate the

ADMR and PM spectra, we measured the P-ADMR spectra at 1010G (full field) and 531 G (half

field), respectively, as shown in Fig. 1. Since the P-ADMR and PM spectra in Fig. 1 are

identical, we conclude that the two PA bands in the PM spectrum are due to photoinduced triplet

transitions. We note that the H-ADMR triplet powder pattern at full field is not simply an

integration display of a standard thermalized triplet LESR lineshape [6], since transition

probabilities as well as changes in the recombination rates among the triplet sublevels, are

involved [16]. However, an accurate measure of the triplet ZFS parameters can be still obtained

by taking the derivative of the H-ADMR spectrum [16]. From the six singularities, shown as

arrows in Fig. 1 lower inset, we calculate for the triplets in C_{60}: T/PS, D = 0.0115 cm^{-1} and

E = 0.0008 cm^{-1}, respectively, identical to the ZFS parameters determined previously by LESR

[6]. The triplet state is thus nearly axially symmetric, of about 6Å in size, i.e., delocalized over

(?)

most of the C_{60} molecule (7Å in diameter). To estimate the triplets life time τ we measured the in-phase of out-of-phase ADMR signals at 1.65 eV, versus the μwave modulation frequency, as shown in Fig. 1 upper inset. Assuming longer spin lattice relaxation than τ [16], we determine τ at 4K to be 5 ms, an order of magnitude longer than in Ref. [6].

The PL spectrum of C_{60}: T/PS is also shown in Fig. 1. It peaks at 1.65 eV [9-12]. Excitation frequency dependence of the PL at 4K shows that it contains a *fast and slow* components. The fast PL is probably due to emission of singlet excitons, whereas the slow component is due to emission of triplet excitons, as determine by its H-PDMR spectrum [12]. As shown in Fig. 1 (lower inset) the H-PDMR and H-ADMR triplet powder patterns are quite similar, however $\delta n < 0$, whereas $\Delta L > 0$. Also the in phase and out-of-phase ADMR and PDMR frequency dependencies are identical (Fig. 1, upper inset). These two measurements show that the μwave induced increase in the triplet recombination rate, which results in $\delta n < 0$ is mostly radiative in nature, in agreement with $\delta L > 0$. In fact from the values of $\delta L/L$ ($\sim 10^{-4}$) and $\delta n/n$ ($\sim - 6 \times 10^{-3}$) we calculate that the triplet PL component is only 1/60 of the total PL signal. This is consistent with our measurements of the PL frequency dependence, separating the slow and fast components.

The PM spectrum of the C_{60} film, however, is much more complicated [10,11] since it contains at least 5 PA features, as shown in Fig. 2 (b). These are PA bands C_1 and C_2 at 0.8 and 2 eV, respectively, T_1 and T_2 at 1.2 and 1.8 eV, respectively, and a derivative-like feature (E) with zero crossing at 2.4 eV. We found in C_{60} films that all PA bands increase as $I_L^{\frac{1}{2}}$,

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indicating a bimolecular recombination kinetics. However the PA bands do not share a common

origin due to their distinctly different laser modulation frequency (f) and temperature (θ)

dependencies. C_1, C_2 and E depend stronger with f than T_1 and T_2 (Figs. 2(a) and 2(b)). Also

T_1 and T_2 have a stronger θ dependence than C_1, C_2 and E; in fact at $\theta = 300$ K (Fig. 2 (c))

T_1 and T_2 completely disappear from the PM spectrum.

The inset of Fig. 2 (c) shows our electro-absorption (EA) spectrum measured at 300 K

on the same C_{60} film, with fields of 20K V/cm, which were modulated at 1 kHz. The EA

spectrum shows strong derivative-like features [10,11] which at their lower energy side are

identical with band E in the PM spectrum. We therefore identify E as due to EA caused by

photogenerated electric fields in the film due to photoinduced charge separation. Since the band

E is more correlated with C_1 and C_2, we tentatively identify C_1 and C_2 PA bands as due to

photogenerated charge carriers; T_1 and T_2 PA bands, on the other hand, are due to neutral

photoexciations. The spin states are analyzed with the following magneto-optical

measurements.

Three typical H-ADMR spectra of C_{60} film measured at different probe photon energies

are shown in Fig. 3. Each spectrum contains two components with opposite signs and different

P-ADMR spectrum (Fig. 3): a broad (powder pattern) component ($\Delta H = 180G$) with $\delta n/n \sim -$

2×10^{-3} and a narrow component ($\Delta H = 15$ G) with $\delta n/n \sim 10^{-2}$. Correlated with the broad

component, centered at H = 1071 G, there is a negative H-ADMR signal at "half field" at H

= 531 G. This clearly identifies the negative ADMR at full field and half fields as $\Delta m_s = \pm 1$

[handwritten: How can you have delocalization of the exciton in the T/PS when you have a single C60 balls separated by (more) the T/PS matrix?]

and $\Delta m_s = \pm 2$ transitions, respectively, associated with ś-wave absorptions of triplet excitons.

Then from the triplet powder patterns we obtain the ZFS parameters of triplets in C_{60} film; they

are D ~ 98 x 10⁻⁴ cm⁻¹ and E ~ 8 x 10⁻⁴ cm⁻¹ respectively. D in C_{60} film is therefore

substantially smaller than in C_{60}: T/PS glass, showing a larger exciton delocalization in the film;

this is probably caused by an increased intermolecular interaction. In contrast, we identify the *[handwritten: (?)]*

narrow, positive ADMR component peaked at 1071 G, as due to spin ½ excitations with g ~

2.000.

The P-ADMR spectra of the S = ½ and S = 1 ADMR components are shown in Fig.

3. The triplet spectrum contains two $\delta n < 0$ bands at 1.1 and 1.8 eV, identical to the T_1 and

T_2 PA bands in the PM spectrum (Fig. 2(a) and (b)); we conclude that the long-lived neutral

photoexciations in C_{60} film are triplet excitons. Their optical transitions in the triplet manifold

are further split compared to the triplets in C_{60}; T/PS glass (Fig. 1), probably due to additional

energy relaxation in the film, consistent with their smaller ZFS parameters that we measured.

Also since T_1 and T_2 PA bands in C_{60} films and glass are both due to triplets, we can calculate

the triplet-triplet annihilation or bimolecular recombination rate b in C_{60} films. This is based on

the triplet steady state density in T/PS glass (N_g) and in film (N_g) the laser excitation intensity

I and the triplet lifetime (τ) in glass, and using the relation $b = N_g/(N_g^2 \tau)$. We obtain b ~

10⁻⁹ cm²/sec, one of the largest exciton bimolecular recombination rate constant measured in

solids.

By contrast, the spin ½ P-ADMR spectrum (Fig. 3) contains three spectral features: two

δn bands at 0.8 and 2.1 eV, respectively, and a derivative - like δn band with zero crossing at 2.4 eV. The δn bands are identical to the C_1, C_2 and E bands of charge carriers in the PM spectrum (Fig. 3 (b) and (c)). Similar (but not identical) optical transitions have been measured in the absorption spectra of C_{60}^* produced by γ irradiation [17], alkali metal doping [18] and charge transfer from semiconductors colloids [19]. We therefore identify the charge carriers as spin ½ C_{60}^*.

We have also measured the PL and its H-PDMR spectrum in C_{60} film. In the C_{60} films, as in glass, the PL at 4K contains also two components; a fast component due to singlet excitons and a slow component due to triplet excitons; both PL components increase as I_L. We measured a positive PDMR with an H spectrum identical to the H-ADMR spectrum at 1.6 eV (Fig. 3, lower inset), which contains only the triplet powder pattern; no spin ½ component was identified in H-PDMR.

Our results for excited states in C_{60} films can be explained by the following scenario: Upon excitation, singlet excitons are formed. Some of them decay radiatively giving rise to the fast PL component with no PDMR signal. However a significant fraction of the singlet excitons decay into the triplet manifold. Fast triplet recombination occurs via bimolecular kinetics, which also may produce charge separation into C_{60}^*. This can explain the seemingly contradictory results for the charge excitations in C_{60} films, in that their density increase as $I_L^½$ but their ADMR signal is positive, indicating geminate recombination [12]. This can be reasonably reconciled assuming that C_{60}^* generation, not recombination, has a bimolecular kinetics. The

long-lived surviving triplets recombine monomolecularly; some of them decay radiatively giving rise to the triplet PL component that we have observed.

An attempt to identify the various transitions in the PM spectrum using the C_{60} energy levels calculation based on CNDO/S, and assuming rigid band approximation, is shown in Fig. 2 (b); the energy levels notation is based on the C_{60} icosahedral point group symmetry [13]. The HOMO (h_u) and LUMO (t_{1u}), both with odd parity u, give rise to a π-π^* forbidden transition which, however, can be enhanced by the EA spectrum (Fig. 3 (c)) [11]. In C_{60} films it appears that this transition is located at 2.4 eV. Then the important C_{60}^- optical transition, (when an electron is added at the LUMO level at t_{1u}) is the C_1 transition ($t_{1u} \rightarrow t_{1g}$) at 0.8 eV, which also appears upon alkali metal doping [18]. Moreover, the important transitions of C_{60}^+ (when a hole is added as the HOMO level at h_u) is the C_2 transition ($g_g \rightarrow h_u$) at 2 eV. The almost rigid band approximation can also explain the two optical transitions associated with the photoinduced triplets. When an electron is promoted to the LUMO level, a hole appears at the HOMO level. If the relaxation energy associated with the excited states in the triplet manifold is relatively small (as depicted in Fig. 2 (b)), then the two triplet transitions T_1 and T_2 are not far from the C_1 and C_2 transitions of C_{60}^*; this is in agreement with the experiment where C_1 and C_2 peak at 0.8 and 2 eV, respectively, whereas T_1 and T_2 are at 1.1 and 1.8 eV, respectively.

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Figure Captions

Fig. 1:   PM, PL and P-ADMR spectra of C_{60}: T/PS glass at 4K; the PA bands T_1 and T_2 are assigned. Lower inset shows the H-ADMR at 1.65 eV (T_1) and the H-PDMR spectra of the PL band at "half" and "full" fields, respectively, upper inset shows the in-phase and out-of-phase ADMR and PDMR signals vs. the μwave modulation frequency.

Fig. 2:   PM spectra of C_{60} film at different modulation frequency f and sample temperature θ. (a) f = 20 kHz, θ = 80 K; (b) f = 20 Hz, θ = 80 K; (c) f = 500 Hz, θ = 300 K. The PA bands C_1, C_2, T_1, T_2 and E are assigned. The inset of Fig. 2 (b) shows the C_{60} energy levels as calculated in Ref. 13; singlet and triplet manifolds are depicted on the left and right hand sides, respectively. The inset in Fig. 2 (c) shows our electro-absorption spectrum, measured on the same C_{60} films; the bands C_2 and E are derived from the PM spectrum based on the EA spectrum in the inset.

Fig. 3:   P-ADMR spectra of the S = ½ (at H = 1071 G) and S = 1 (at H = 1050 G) components of the ADMR signal. The bands C_1, C_2, T_1, T_2 and E are as in Fig. 2; C_2 and E bands are derived from the ADMR spectrum as in Fig. 2 (c). Three typical H-ADMR spectra at 0.8, 1.6 and 2.3 eV, respectively are also shown to demonstrate the two ADMR components in the spectrum: the broad, negative component is due to triplets, whereas, the narrow, positive component is due to S = ½ photoexcitations.

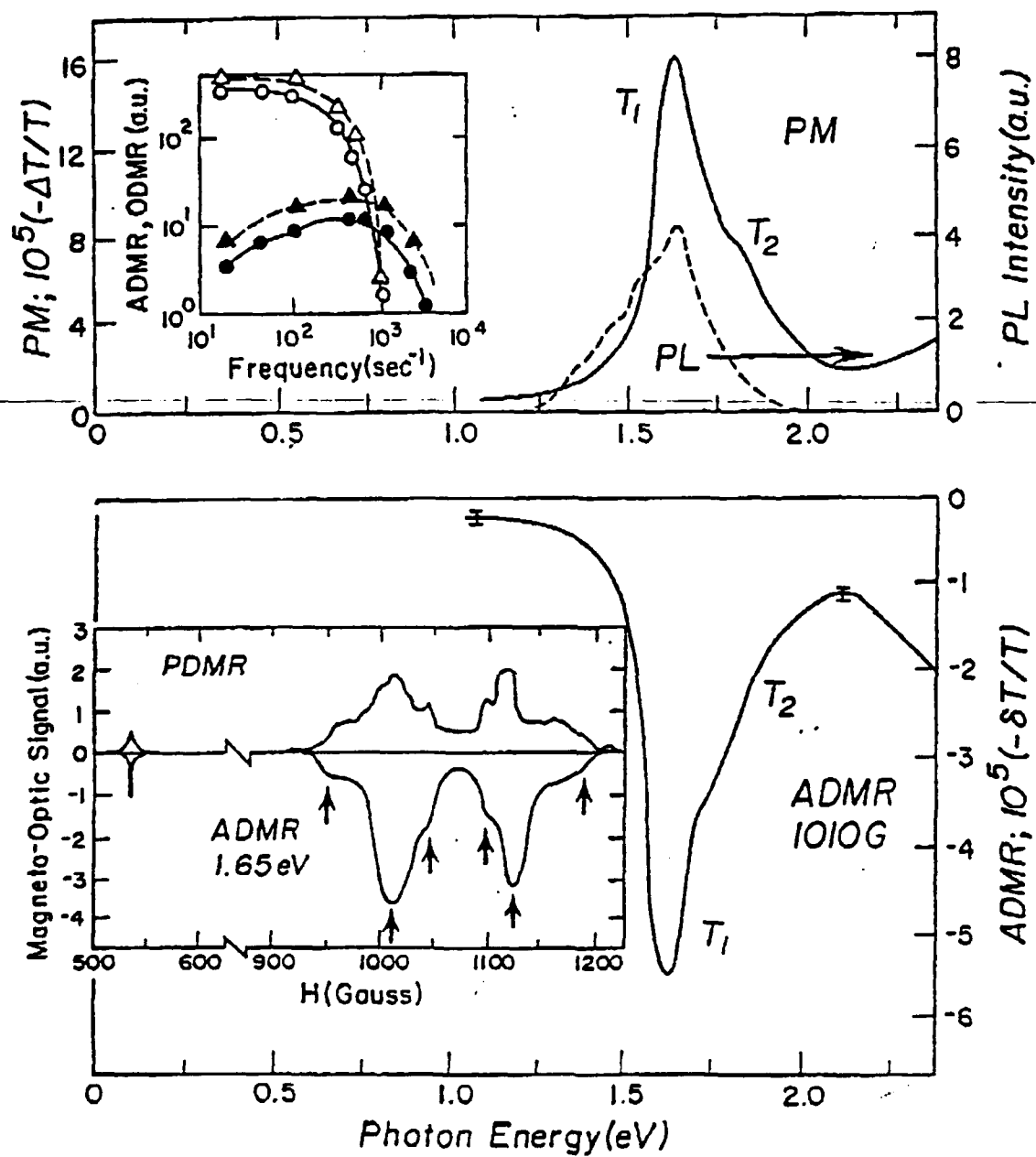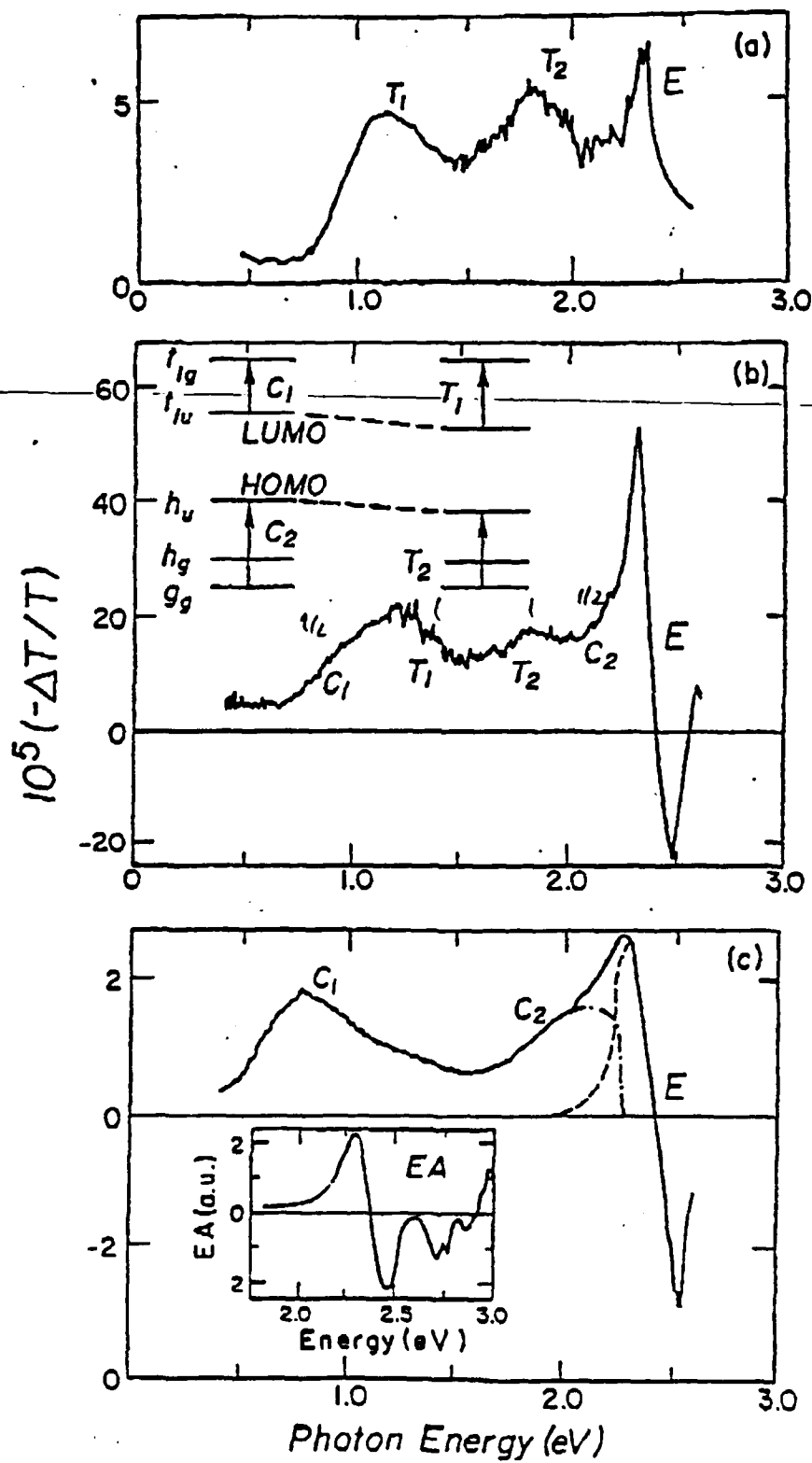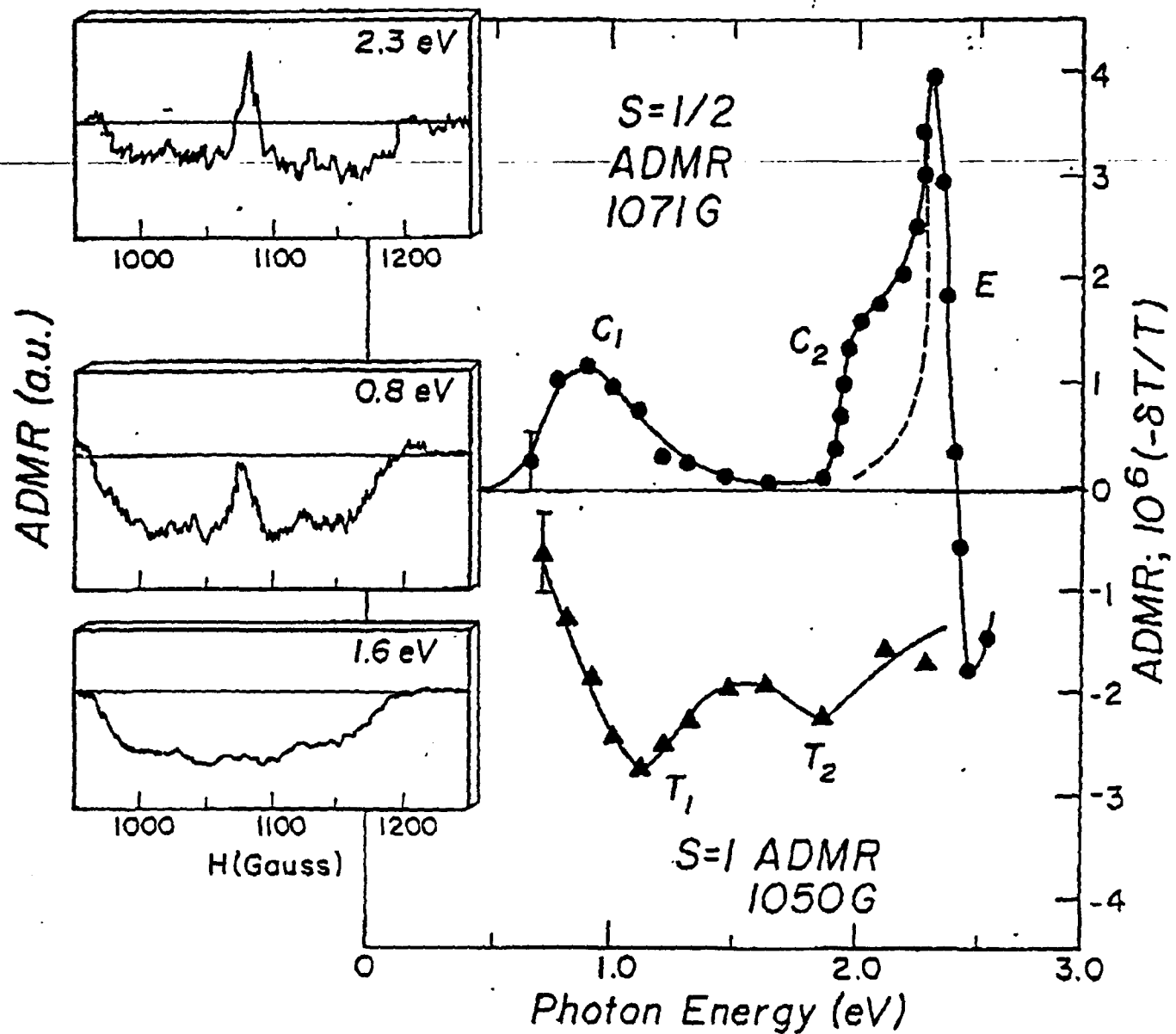Fig. 1

Fig. 2

Fig. 3

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